

Lattice instabilities in cubic pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$

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The oxide pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ is in some ways analogous to perovskite PbTiO_3 , in that $\text{Bi}_2\text{Ti}_2\text{O}_7$ has two cations, Bi^{3+} and Ti^{4+} in oxidation states that are normally associated with a propensity to off-center. However, unlike PbTiO_3 , $\text{Bi}_2\text{Ti}_2\text{O}_7$ is experimentally observed to remain cubic down to 2 K, while the only observed ionic displacements are local and incoherent. Here we report first-principles calculations of the zone-center phonons of the ordered cubic pyrochlore which reveal several lattice instabilities. An analysis of the structural energetics suggest that the ordered cubic pyrochlore is unstable with respect to distortion towards a ferroelectric ground state with a large polarization. Our results suggest a key role of a frustrated soft polar mode in the dielectric properties of bismuth pyrochlores.

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Chemical disorder has been effectively used as a means of inhibiting structural phase transitions and thereby controlling the dielectric properties in the ABO_3 perovskites. This has engendered the class of relaxor ferroelectrics with high and relatively temperature-stable dielectric constants.^{1,2} Another path to obtaining new materials with inhibited phase transitions is through structural, rather than compositional, frustration. This is in analogy with magnetic systems where frustration can be achieved through substitution (spin glass) or through lattice geometry (spin ice).³ Recently the bismuth pyrochlores have been suggested as potentially belonging to the class of geometrically frustrated polar materials.⁴

$\text{A}_2\text{B}_2\text{O}_7$ pyrochlores in the $\frac{1}{2}\text{Bi}_2\text{O}_3\text{-ZnO-}\frac{1}{2}\text{Nb}_2\text{O}_5$ (BZN) system^{5,6} have received considerable attention for capacitor applications due to their high dielectric constant (~ 150), low loss, and absence of any structural phase transition. At low temperatures, dielectric relaxation behavior similar to what is observed in relaxor ferroelectrics is found. Thin films have been shown to retain the high dielectric constant of their bulk counterparts while also displaying a high tunability with applied electric field^{7,8} suggesting that these materials could easily find applications.

The pyrochlore formula can be written $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ to highlight the view of the cubic $Fd\bar{3}m$ structure as two interpenetrating networks; the one of $\text{A}_2\text{O}'$ comprises corner-connected $\text{O}'\text{A}_4$ tetrahedra, and the other of B_2O_6 comprising corner connected BO_6 octahedra as shown in Fig. 1. In the ideal pyrochlore structure, the atoms occupy special Wyckoff positions in the unit cell, A (0,0,0), B ($1/2, 1/2, 1/2$), O' ($1/8, 1/8, 1/8$), except O, which is found at ($1/8, 1/8, z$).⁹ In BZN partial substitution of Zn on the Bi A-site occurs and is accompanied by the appearance of seemingly uncorrelated and random displacements of Bi (and O') atoms off the ideal pyrochlore site.^{10,11,12} Even in the absence of cation substitution on the Bi site, pyrochlores such as $\text{Bi}_2\text{Ru}_2\text{O}_7$, $\text{Bi}_2\text{InNbO}_7$, and $\text{Bi}_2\text{CrTaO}_7$ have been shown to accommodate sig-

nificant static disorder in the $\text{A}_2\text{O}'$ network, the cause of which has been suggested to originate in the Bi^{3+} lone-pair. The static disorder in this structure type is thought to be responsible for both the high and tunable dielectric constant as well as the relaxor-like dielectric relaxation yet its precise role remains unclear. This has stimulated interest in understanding the role of polar phonon modes in the dielectric properties of bismuth pyrochlore oxides.¹³

It is clearly advantageous to study a chemically homogeneous system in order to separate the role of compositional disorder from geometry. In this contribution, we report first-principles calculations of the zone-center phonons of the ideal cubic pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ as a first step towards understanding the origins of the static displacive disorder and its possible effects on the polar properties. Similar to other bismuth pyrochlores,¹⁰ in the bis-

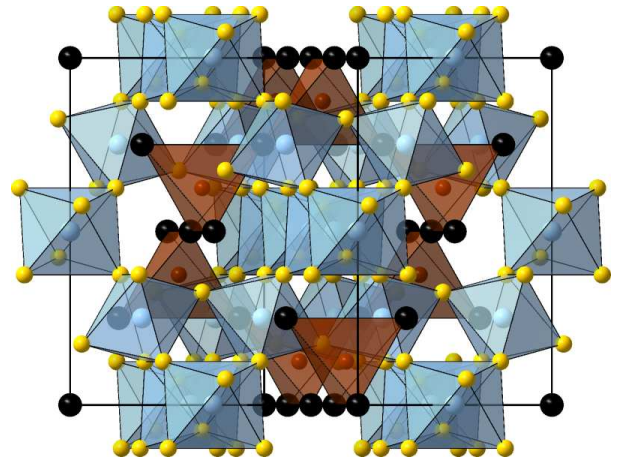


FIG. 1: Color online: $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ pyrochlore crystal structure showing interpenetrating corner-connected networks of $\text{O}'\text{A}_4$ tetrahedra, and BO_6 octahedra. The atom colors are black: A, light blue: B, yellow: O, and dark orange: O' .

TABLE I: Infrared-active, Raman-active, and silent phonons frequencies, ω (cm^{-1}) of ideal cubic pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$, space group: $Fd\bar{3}m$ (No. 227).

Infrared		Raman		silent	
Mode	ω	Mode	ω	Mode	ω
$T_{1u}(1)$	<i>i</i> 98	$T_{2g}(1)$	278	$E_u(1)$	<i>i</i> 100
$T_{1u}(2)$	81	E_g	369	$E_u(2)$	107
$T_{1u}(3)$	112	$T_{2g}(2)$	414	$E_u(3)$	400
$T_{1u}(4)$	229	A_{1g}	462		
$T_{1u}(5)$	262	$T_{2g}(3)$	535		
$T_{1u}(6)$	352	$T_{2g}(4)$	462		
$T_{1u}(7)$	464				

mut titanate pyrochlore, the Bi atoms have been shown to displace incoherently by $\sim 0.4 \text{ \AA}$ in such a way as to occupy a more general Wyckoff position (x, x, z) while retaining average cubic symmetry.¹⁴ Thin films of the recently prepared compound $\text{Bi}_2\text{Ti}_2\text{O}_7$ possess dielectric properties similar to BZN, although they do not seem to be as field tunable at room temperature.¹⁵ Here we show that in the absence of static disorder cubic $\text{Bi}_2\text{Ti}_2\text{O}_7$ has two zone-center lattice instabilities. These couple to produce a low-energy ferroelectric structure with a spontaneous polarization comparable to perovskite ferroelectrics. We also find that the computed displacement of the Bi ion remarkably similar in magnitude and direction to the measured incoherent distortion.

First-principles density functional calculations using projector augmented wave potentials were performed within the local density approximation as implemented in the VASP program.^{16,17} The wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a $6 \times 6 \times 6$ Γ -centered k -point mesh. Phonon frequencies and eigendisplacements were calculated using the direct method where each symmetry adapted mode^{18,19} was moved by approximately 0.01 \AA . Born effective charge tensors were calculated by finite differences of the polarization using the modern theory of polarization²⁰ as implemented in VASP.

We performed full structural optimization of $\text{Bi}_2\text{Ti}_2\text{O}_7$ in the cubic pyrochlore structure, space group $Fd\bar{3}m$, with all ions in their ideal Wyckoff positions. In the absence of incoherent static disorder in the $\text{Bi}_2\text{O}'$ network, we can investigate the tendency for $\text{Bi}_2\text{Ti}_2\text{O}_7$ to distort coherently by calculating the phonon dispersion. Here we focus on a subset of such distortions by constructing the dynamical matrix from finite differences of the Hellmann-Feynman forces at $\vec{q} = 0$ (zone-center) a useful starting point as these modes are directly relevant to the dielectric properties. Table I displays the calculated infrared, Raman, and selected Silent zone-center phonon frequencies and mode assignments. We find two types of very unstable modes (as indicated by the large imaginary phonon frequency $\sim i100 \text{ cm}^{-1}$). The two-

TABLE II: Possible low-symmetry, ordered structures of the ideal cubic pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$, space group $Fd\bar{3}m$. The total energy per formula unit $\Delta E/\text{f.u.}$ (meV) is given relative to the ideal cubic structure. The direction $\hat{\mathbf{P}}$ and magnitude $|\mathbf{P}|$ ($\mu\text{C}/\text{cm}^2$) of the spontaneous polarization is indicated for the structures that are ferroelectric.

Space Group	Irrep	$\hat{\mathbf{P}}$	$ \mathbf{P} $	ΔE
$I4_1md$	T_{1u}	[001]	40	-92
$Ima2$	T_{1u}	[110]	40	-107
$R3m$	T_{1u}	[111]	40	-78
Cm	$T_{1u}+E_u$	[11 δ]	20	-240
$I\bar{4}m2$	E_u	-	-	-90
$I4_122$	E_u	-	-	-83

fold degenerate E_u mode is an antiferrodistortive mode that breaks inversion symmetry, though without creating a polar axis. The freezing in of this mode would lead to any of the following piezoelectric (but not pyroelectric) space groups^{19,21} depending on anharmonic contributions: $I\bar{4}m2$, $I4_122$, or $F222$. The three-fold degenerate T_{1u} mode is a proper ferroelectric mode which when frozen-in would lead to any one of the following space groups: $I4_12d$, $Ima2$, $R3m$, Cm , Cc , $P1$. In either unstable mode, the nature of the eigendisplacements consist, in real-space, of Bi ions moving perpendicular to the direction of the $\text{Bi-O}'$ bond, although in both cases a small cooperative motion of the O network is essential as we discuss below. Note this should be contrasted with the nearly unique and somewhat ill-described ferroelectric pyrochlore $\text{Cd}_2\text{Nb}_2\text{O}_7$ where first-principles calculations show that the unstable T_{1u} mode is mostly Nb-O character while the E_u mode is stable.²² In the E_u case local dipoles are created which cancel when averaged over the unit cell while in the T_{1u} case they add to give a spontaneous polarization. Interestingly, the direction of the Bi ion displacement in both unstable modes is in the direction of the experimentally observed static displacements.

The phonon calculations tell us that at $T = 0$, the ideal cubic pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ is indeed unstable and quite possibly a ferroelectric. To identify which low-symmetry phase is the most energetically favorable we performed a series of structural relaxations within each of the five highest symmetry isotropy subgroups consistent with the freezing in of one T_{1u} or E_u mode. We also considered one lower symmetry structure in space group Cm corresponding to a rotation of the polarization along [11 z]. The results are shown in Table II. We found that the lowest energy structure is ferroelectric, in the polar monoclinic space group, Cm , consistent with the freezing-in of both a [110] T_{1u} mode and an E_u mode. For this structure, we calculate a substantial polarization of $\mathbf{P} \approx 20 \mu\text{C cm}^{-2}$, and although the polarization can freely rotate along [11 z] it remains nearly along [110].²³

In Fig. 2, we compare the $\text{Bi}_2\text{O}'$ networks in the cubic

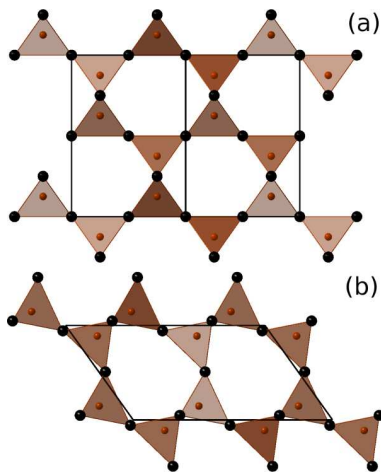


FIG. 2: Color online: (a) Bi₂O' network of the cubic Bi₂Ti₂O₇ structure. This is the sub-lattice of the structure associated with unstable phonon modes. A Projection of the Bi₂O' sublattice of the relaxed *Cm* structure. The outline of the monoclinic unit cell is shown.

structure and in the *Cm* structure. In the *Cm* structure we find the average displacement of Bi and O' atoms away from the cubic Wyckoff positions to be 0.37 Å and 0.13 Å respectively. Curiously these coherent displacements are remarkably similar in magnitude to the incoherent Bi and O' displacements experimentally determined to be 0.43 Å and 0.16 Å respectively. It is tempting to consider this agreement as suggesting what is being measured is in some sense an average structure consisting of coherently distorted nanodomains formed by the freezing-in of extremely localized, cooperative modes²⁴. (A signature of this effect can be found from first-principles phonon calculations by the appearance of an extremely flat unstable phonon branch²⁵ at $T = 0$; such calculations are underway.) But we stress, both the T_{1u} and the E_u modes contain significant O-character. In the *Cm* structure for example, O atoms displace from their high-symmetry Wyckoff position on average by ≈ 0.1 Å, while O-sublattice displacement has not been observed experimentally.

So the question remains as to why incoherent static distortions in the Bi₂O' network are observed in neutron studies (from growth temperatures down to 2 K) rather than a structural transition into one of the distorted/ferroelectric phases suggested above. Although we do not answer this question here, it is clear that these apparent incoherent distortions are not stable in the ground state as all of the zero-temperature diagonal elements of the dynamical matrix at $\vec{q} = 0$ were positive.

This implies for example that the Bi and O' sublattices by themselves are stable^{26,27} and highlights the key role played by the O-sublattice in the calculated instability.

The origin of the disorder aside, our first-principles results suggests that the key in regard to understanding the dielectric properties is a frustrated polar soft mode. In Bi₂Ti₂O₇, the unstable ferroelectric mode and the disorder involve the same ions and a strong coupling between the two distinct structural modes is expected.^{28,29} If we take for a given the presence of frozen-in Bi and O' disorder, one can imagine an analogous situation to perovskite relaxor ferroelectrics where intentionally doped chemical disorder frustrates long-range ferroelectric order. Further experiments are suggested to elucidate this frustrated state in Bi₂Ti₂O₇. In analogy with the perovskite relaxors ferroelectrics, the effect of cooling in a strong electric field should be investigated – can a structural transition be observed? If indeed the ground state is ferroelectric and the picture of geometric frustration of an infrared-active phonon is valid, then there should be a significant downshift of spectral weight observable with optical spectroscopy.³⁰ Such a downshift of spectral weight should also manifest in the low-temperature heat capacity.³¹

In summary, we have shown that the ideal bismuth titanate pyrochlore is unstable towards coherent lattice distortions at $T = 0$, the ground state being ferroelectric with Bi and O' ion displacements off the ideal cubic pyrochlore lattice equal in magnitude to the measured incoherent distortions. Although it is still an open question, the results presented here suggest that the interaction between the static disorder and the soft ferroelectric mode are responsible for the unusual dielectric properties of bismuth pyrochlores.

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